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INTRODUCTION

Nitrification and denitrification have been well-recognized phenomena in wastewater treatment for many years. The former occurred to the greatest degree during the warmer months of the year and was considered highly beneficial in most instances because of the oxygen resource that the nitrates provided. Because of additional capital and operating costs required to produce nitrates, American engineers generally attempted to design or use processes that minimized nitrification.

The problems of rising sludge in conventional activated-sludge and standard-rate trickling-filter plants were shown to be due to denitrification. The common way of controlling the problem was to limit nitrification.

The Michigan studies on the significance of nitrogenous oxidation (NOD) in creating oxygen sag in receiving streams and other studies showing the role of ammonia and nitrate nitrogen in stimulating algal blooms have demonstrated the need for information on how wastewater-treatment plants can be designed to accomplish nitrification and denitrification. Figure 1 shows the facilities required to accomplish both in a controlled manner.

A three-stage biological system is considered necessary in northern climates where wastewater temperatures drop below 65° F (18° C). The first stage is necessary to remove carbonaceous BOD_5 to levels of about 50 mg/l. The second stage is needed to accomplish nitrification and should be designed to employ the plug-flow principle as closely as possible. The third stage accomplishes denitrification. A source of carbonaceous BOD must be added to reduce the nitrates to nitrogen gas in a reasonable period of time.

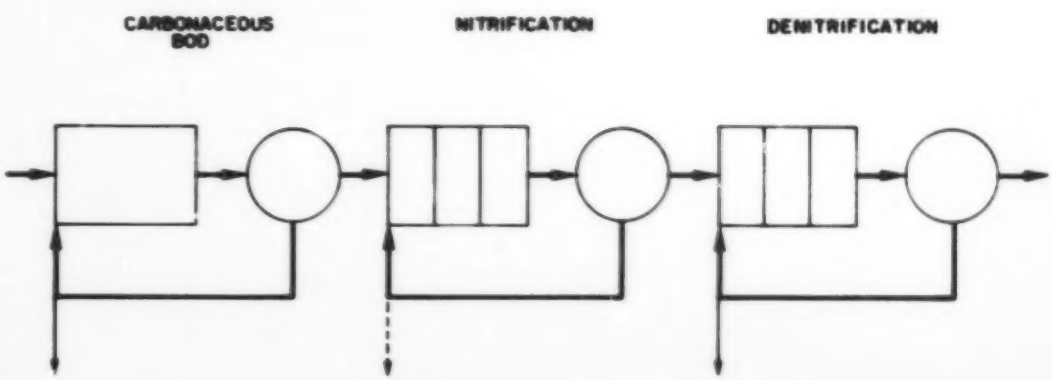

Figure 1. Model system for nitrification and denitrification.

Chapter 1

FACTORS AFFECTING NITRIFICATION KINETICS

The nitrification phenomenon has been studied intensively by soil scientists for the past century. With the advent of biological wastewater-treatment systems, chemists and engineers were impressed by the fact that the same phenomenon occurred in their treatment plants. Originally, in the absence of biological methods of assessing degrees of purification, chemical analyses served as the major means of evaluation. Experience soon taught that highly nitrified effluents were immune to putrefaction. As a result, wastewater-treatment plants before 1930 were designed as standard or conventional plants intended to accomplish a relatively high degree of nitrification, at least during the summer months.

With the development and widespread application of the BOD (biochemical oxygen demand) test, it became apparent to many designing engineers that high degrees of waste treatment, in terms of BOD removal, could be accomplished at marked savings in capital and operating costs by designing to avoid nitrification. Thus, from 1940 until the late 1960's the main objective in the United States was to design to minimize nitrification.

Many of the newly designed high-rate or modified plants, and some older plants suffering from overloads, were plagued with denitrification and resultant "rising-sludge" problems in the final clarifiers. These problems stimulated numerous studies on how to control nitrification, since it was a physical impossibility to accomplish high degrees of nitrification, in most cases, without expansion of the plant facilities.

Although the NOD of unnitrified effluents was well understood, sanitary engineers usually dismissed this matter from their minds on the basis of three premises.

- Nitrification is caused by special organisms, the population of which is minimal in surface waters.
- The reaction constant for nitrogenous oxidation is small in relation to the constant for carbonaceous matter.
- Oxidation of ammonia to nitrates simply converts dissolved oxygen to a form from which it is still available to prevent formation of anaerobic conditions.

The philosophy that unnitrified effluents are not damaging to receiving streams has been undermined by biologists and conservationists, who point out that nitrates will not satisfy the oxygen requirements of fish and many other aquatic organisms, and by the river and stream investigations of Gannon[1] and of the Michigan Water Resources Commission, reported by Courchaine.[2]

As a result of the studies conducted in Michigan, many States are now requiring that NOD be considered as well as BOD in any analysis of pollutional loads that streams can bear. This requirement will undoubtedly mean that many plants of the future will be designed to accomplish extensive nitrification, at least during the warmer months of the year when oxidation rates are highest and stream flows are apt to be minimal.

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With regard to eutrophication of surface waters, nitrogen in the fixed forms of ammonium and nitrate ions is considered to be one of the major nutrients supporting blooms of green and non-nitrogen-fixing blue-green algae. Nitrogen removal from wastewaters is being requested in some areas and considered in many others. Where discharge is to lakes or reservoirs with significant detention times, seasonal removal will not suffice and performance 365 days per year will be expected. Removal through nitrification followed by denitrification represents the most promising method at this time. It has the advantage of returning nitrogen to the atmosphere in its natural form.

NITRIFICATION AND POPULATION DYNAMICS

It seems certain at this time that nitrification will play a greater and greater role in wastewater treatment in the future because of anticipated increased NOD-removal requirements and possible use of systems employing nitrification-denitrification for nitrogen removal.

It is conceivable that NOD removal will be a seasonal requirement in most locations and will occur during the warm months of the year. If so, then conventional designs of biological systems similar to those used before 1930, or those capable of maintaining conditions so that the reciprocal growth rate of the nitrifying bacteria is less than the mean cell residence time or sludge-retention time as described by Jenkins and Garrison,[3] will be required. In simple terms, this means that nitrification in plants can be maintained only when the rate of growth of nitrifying bacteria is rapid enough to replace organisms lost through sludge wasting. When these bacteria can no longer keep pace, the ability to nitrify decreases and may become extinct.

It has been well established that no treatment plants, including those of the extended aeration type, are capable of accomplishing complete nitrification, year round, in our Northern States. In situations where nitrogen removal is required and the nitrification-denitrification route is preferred, it will be mandatory to accomplish nitrification in a separate biological system where the reciprocal growth rate can be kept less than the mean cell residence time at all times. Owing to this necessity a large part of the normal BOD will have to be removed before the wastewater enters the nitrification unit. A system for such removal is shown as figure I-1. It is believed that a BOD of 40 or 50 mg/l can be tolerated in the feed to the nitrification unit; consequently either high-rate activated-sludge or trickling-filter systems should be acceptable for the first stage of treatment.

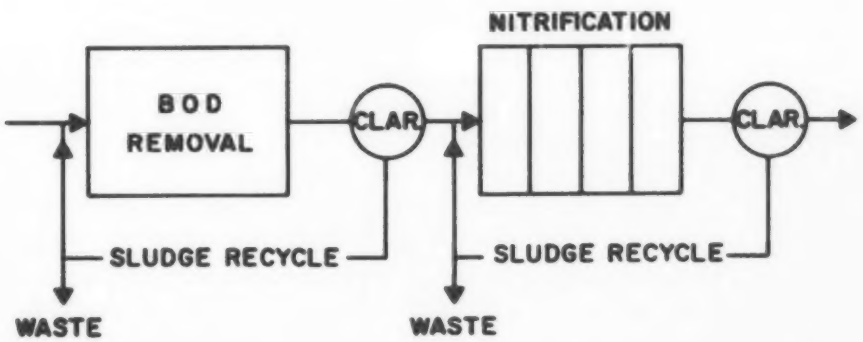

Figure I-1. Two-stage biological system required to guarantee complete nitrification.

NITRIFICATION KINETICS

The response of both nitrite- and nitrate-forming bacteria in pure culture to various environmental conditions has been studied extensively. The effect of pH on the respiration rate of *Nitrosomonas*, as reported by Meyerhof[4] and Engel and Alexander,[5] is shown in figure I-2; the effect on *Nitrobacter*, as reported by Meyerhof,[6] is shown in figure I-3.

Early studies on nitrification in wastewater treatment were related mainly to its control to prevent rising-sludge problems in the activated-sludge process. These studies brought dissolved oxygen (DO) under close scrutiny, since DO was the only environmental condition that could be considered readily controllable under normal operating conditions. Bragstad and Bradney[7] reported that DO must be kept below 0.5 mg/l to control nitrification. Recently, Downing et al.[8] and Jenkins and Garrison[3] have reported on other aspects affecting nitrification, and Zanoni[9] investigated the effect of temperature on the velocity constant for nitrification in treated effluents.

A portion of this study was prompted by three major considerations.

- A paper by Borchardt[10] indicated that temperature had little effect on nitrification in the range of 15° to 35° C (see fig. I-4), in opposition to published data.[11]
- Information is lacking on sludges in systems receiving feed stock containing relatively low BOD.
- There is a considered need to establish a quantitative basis for evaluating the ability of nitrifying sludges to convert ammonia to nitrate under various temperature and pH conditions.

INVESTIGATIONS

Method of Study

The investigations to be described were conducted at Marlborough, Mass., where a 10-gpm pilot nitrification unit, receiving settled high-rate trickling-filter effluent, was operated, open to the weather from October 1969 through April 1970. All observations on the effects of DO were made in the pilot plant. The studies on the influence of temperature and pH were made in the laboratory using return sludge from the nitrification unit and settled trickling-filter effluent in the apparatus shown in figure I-5. The batch studies on pH and temperature were conducted with DO levels above 2 mg/l to insure that DO would not be an inhibiting factor.

Experimental Results

Pilot Plant. The results of measuring the DO in the aeration tank of the pilot plant and the resulting effluent quality are indicated on figure I-6. The DO concentration was measured twice daily and found not to have a significant variance during any given day. The effluent ammonia-nitrogen concentration was taken from a 24-hour composited sample.

The wide range of DO concentration resulted from breakdowns in one of the two available compressors and from a varying demand for air at other locations.

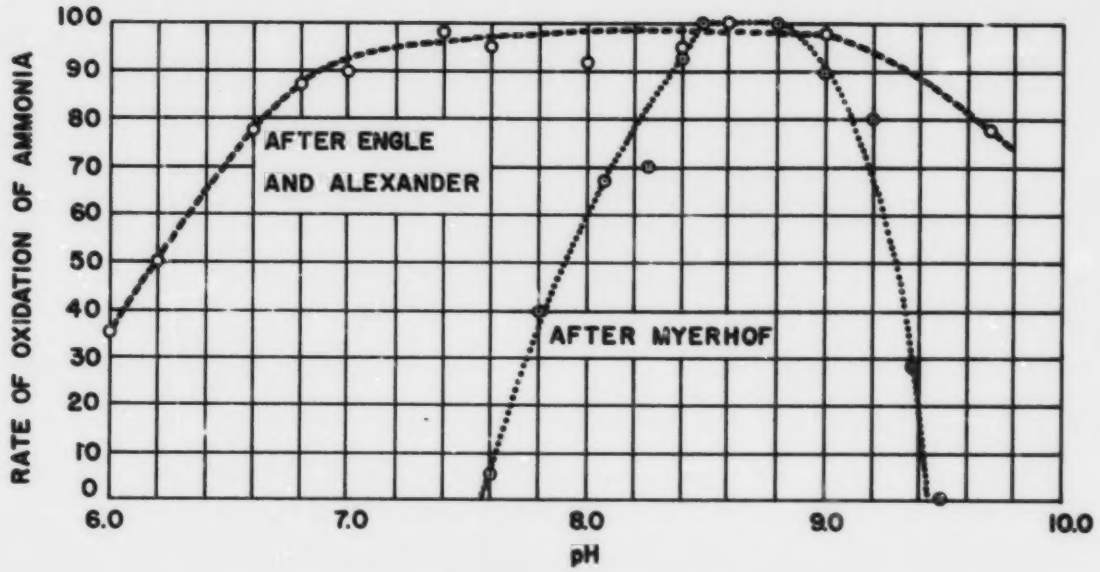

Figure I-2. Effect of pH on oxidation of ammonia by *Nitrosomonas.*

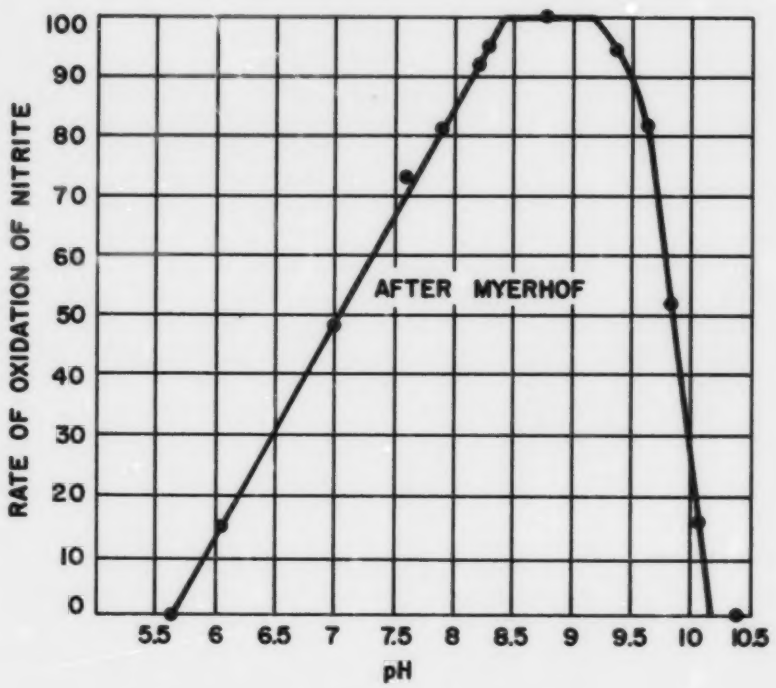

Figure I-3. Rate of oxidation of nitrate by *Nitrobacter.*

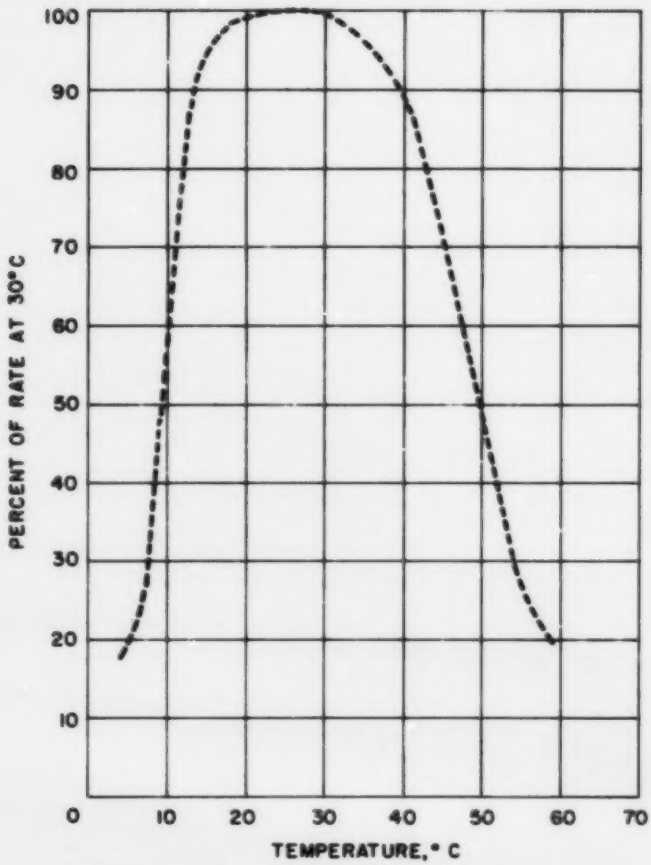

Figure I-4. Effect of temperature on nitrification as reported by Borchardt.[10]

Figure I-6 indicates that there was apparently no inhibition of nitrification occurring at DO levels exceeding 1 mg/l.

Laboratory. The laboratory studies were concerned with determining the effect of temperature and pH under carefully controlled conditions. The procedure used involved collection of samples of return sludge from the nitrification pilot plant and of settled trickling-filter effluent, determination of suspended and volatile suspended solids in the return sludge, and adjustment of portions of each to definite pH and temperatures before making the desired mixtures in the aeration units. In most instances, the trickling-filter effluent was supplemented with a dilute aqueous solution of ammonium chloride in order to give runs of sufficient duration to obtain three or more experimental values.

The rate of nitrification was determined by measuring residual ammonia nitrogen on grab samples of mixed liquor that were filtered immediately after collection. DO, pH, and temperature were monitored continuously during the course of each study. Dilute sodium hydroxide was added to control pH as needed. The system of study may have involved some slight loss of ammonia at pH levels above 8.5, but such losses were too insignificant to be detected from a plotting of the data.

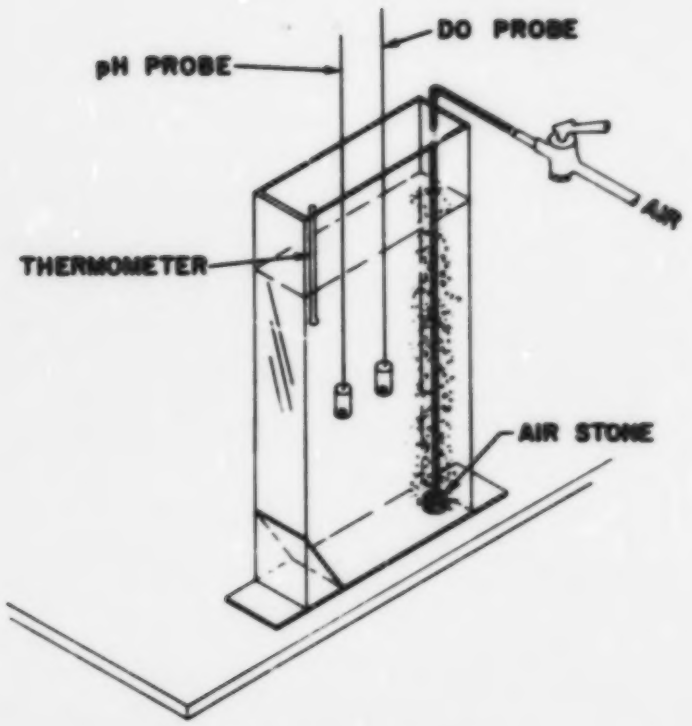

Figure I-5. Laboratory aeration unit.

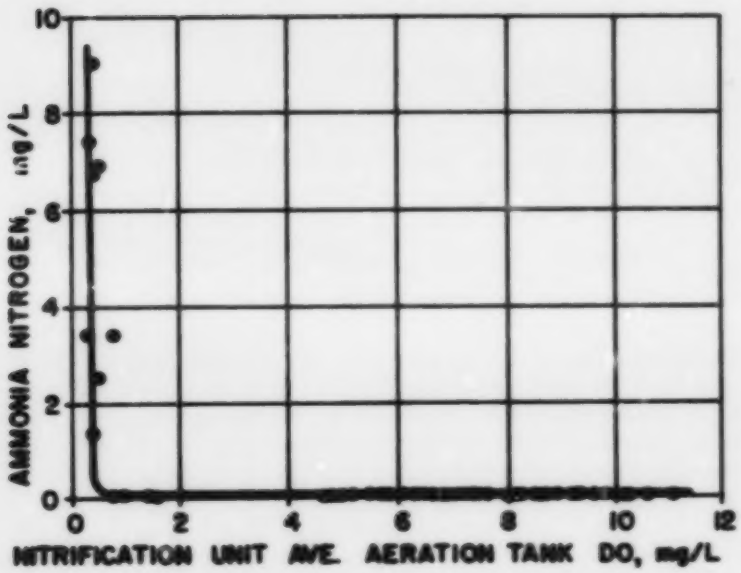

Figure I-6. Relationship of residual ammonia to dissolved oxygen.

It was assumed that the relative population of nitrifiers in the total MLVSS (mixed-liquor volatile suspended solids) concentration for the duration of the study remained constant. It is felt that this assumption was justified due to the long duration of the pilot studies run under the same conditions, employing settled trickling-filter effluent as feed stock.

MLVSS. The nitrification studies were conducted with MLVSS concentrations within the range of 800-6,000 mg/l.

A sample of two of the experiments run at the same pH and temperature conditions but with two different mixed-liquor volatile suspended solids is shown in figure I-7. It was observed that the time to completely nitrify the same amount of ammonia nitrogen per gram of MLVSS was constant given the same environmental conditions. This observation allows direct comparisons to be made for different MLVSS concentrations in the study and permits subsequent data to be expressed in terms of milligrams of ammonia nitrogen per milligram of MLVSS.

Ammonia. The augmented ammonia-nitrogen concentrations for the studies varied from 6 to 60 mg/l. The ammonia-nitrogen concentration had to be augmented on many occasions because the time required for complete nitrification of low levels was so short that only one or two samples could be analyzed before attaining the zero level. Two sample results are shown in figure I-8. Both of the experiments were conducted at the same pH and temperature conditions. As can be seen from the figure, the slopes of the lines are parallel and constant for all residual concentrations of ammonia nitrogen regardless of the initial concentration. This result would indicate that nitrification

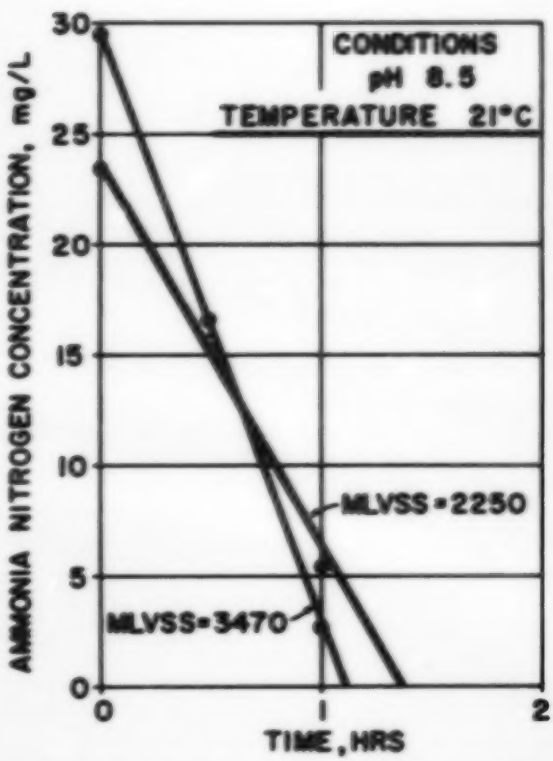

Figure I-7. Effect of variation in mixed-liquor volatile suspended solids.

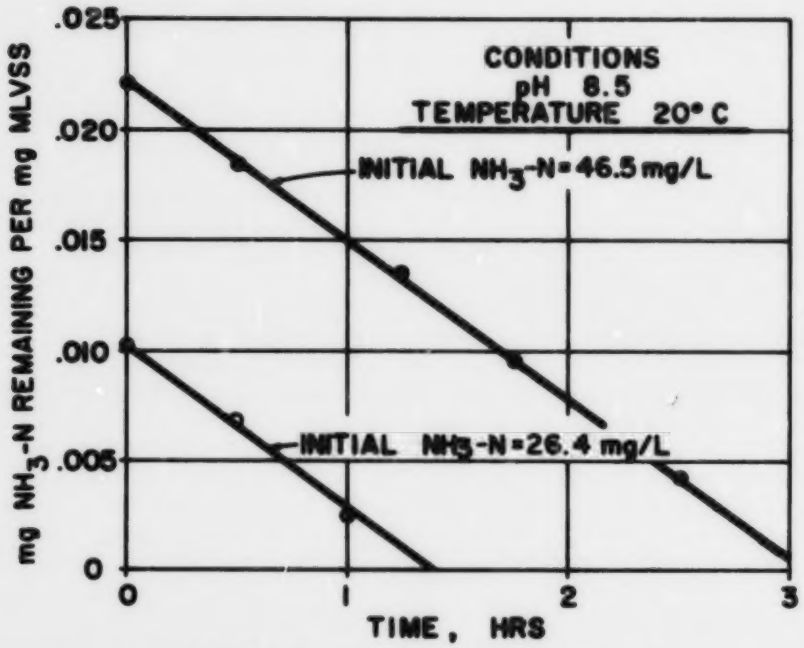

Figure I-8. Effect of variation in ammonia concentration.

is not inhibited at concentrations normally found in a domestic wastewater system, and also allows adjustment of other data for different ammonia-nitrogen concentrations by constructing a line parallel to the experimental line at the desired concentration.

BOD. A special study was made to determine the effect of variable BOD upon the rate of nitrification. In the study three different samples were nitrified. The temperature and pH for all three units were the same. The wastewater in the first unit was primary effluent with a BOD of 110 mg/l. The second unit contained settled trickling-filter effluent with a BOD of 45 mg/l. The third unit contained nitrification effluent from the pilot plant with a BOD of 5 mg/l. All samples were augmented with enough ammonium chloride to give a reasonable duration of the test.

Figure I-9 shows the results of this special study. Within the limits of the study, there was no apparent inhibition of nitrification for the various BOD concentrations. It should be realized that this study was undertaken to determine the reaction of the nitrifiers to a shock loading of BOD, and that any sustained high-BOD loading would eventually cause nitrification to cease, owing to the washing-out effect of sludge wasting on the nitrifiers. This conclusion was reached because of the low growth rate exhibited by the nitrifiers as compared to those organisms utilizing carbonaceous BOD and because of the established fact that an increased BOD loading in a conventional system leads to greater sludge production.

pH. The pH range investigated in these studies was from 6.0 to 10.5. The samples were adjusted to the desired pH level and maintained at that level for the duration of the experiment. The ammonia-nitrogen weight per MLVSS weight ratio of the grab samples was plotted against time, and all the other variables were noted. The time plot allowed calculation of the exact time of complete nitrification, i.e., complete oxidation of ammonia. A sample graph (see fig. I-10) shows two sample results, both of which were obtained at a temperature of 20° C. The pH of one

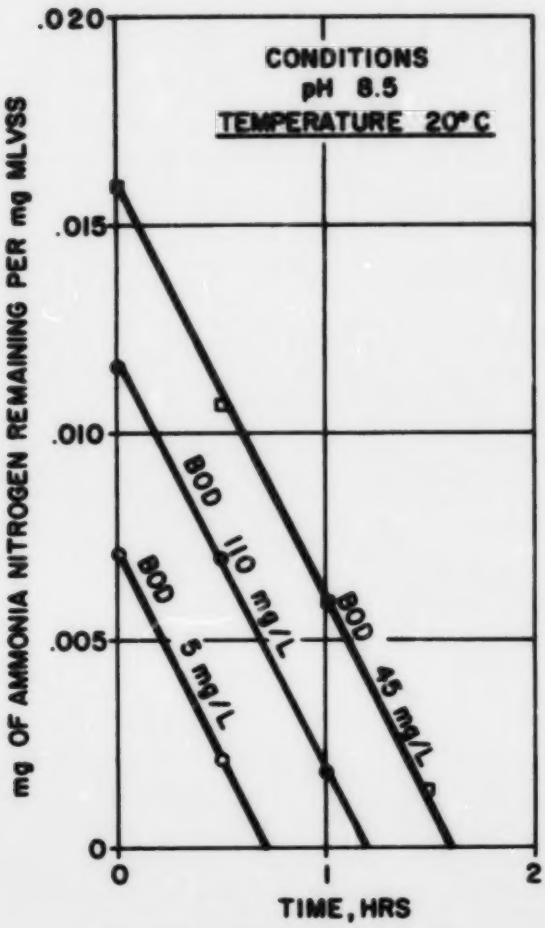

Figure I-9. Effect of variation in BOD.

sample was 8.5 and the other 6.5. The figure also shows an adjusted line to compensate for different initial concentrations of ammonia.

Three factors are immediately evident from figure I-10.

- There was no apparent initial uptake of ammonia nitrogen by the nitrifiers.
- There was no lag time involved in the rate of nitrification.
- The rate was uniform and constant for the entire length of the experiment. This result indicates that the nitrifiers work at maximum efficiency at all times independent of the residual concentration of ammonia nitrogen.

The studies indicate an optimum pH for nitrification to be 8.4. Figure I-11 shows that 90 percent of the maximum rate occurs in the range of 7.8 to 8.9, and that outside the ranges of 7.0 to 9.8 less than 50 percent of the optimum rate occurs.

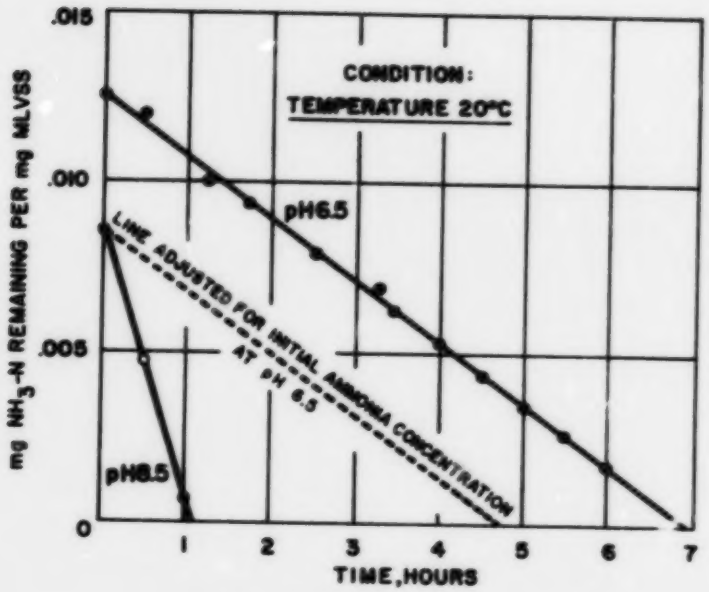

Figure I-10. Effect of variation in pH.

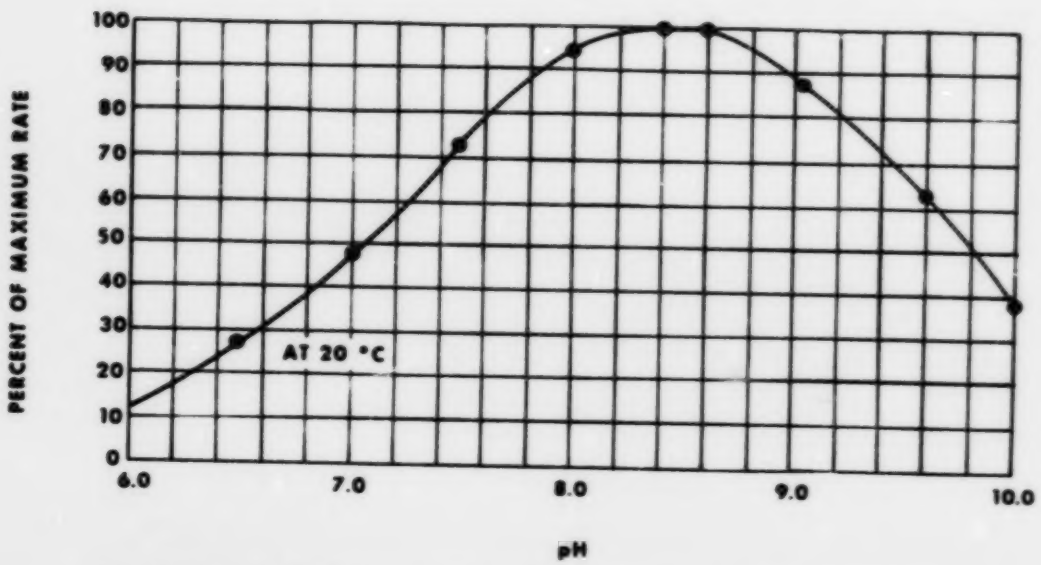

Figure I-11. Percent of maximum rate of nitrification at constant temperature versus pH.

Temperature. The temperature studies covered the range from 5° to 30°C, and nitrification occurred at all temperatures investigated. The rate of nitrification increased with temperature throughout the full range. Figure I-12 indicates the straight-line relationships for two sample experiments run at different temperatures but the same pH. One adjusted line is shown to offset the initial ammonia concentration difference. There was no lag period observed nor any decrease in the rate of nitrification as the residual ammonia concentration decreased.

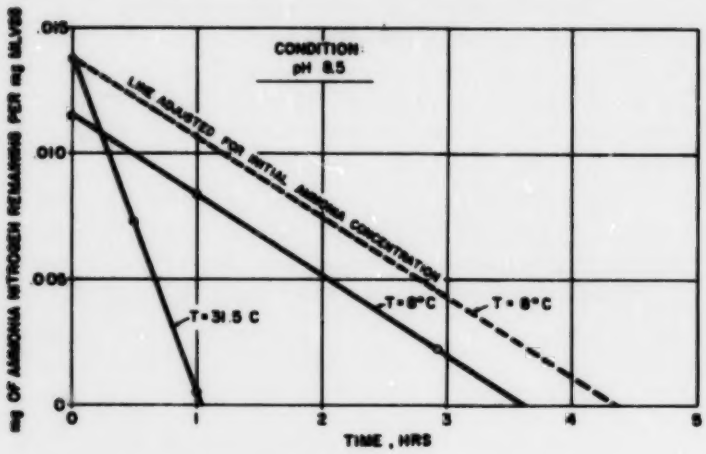

Figure I-12. Effect of variation in temperature.

Figure I-13 indicates the relationship of the rate of nitrification at all temperatures studied to the rate at 30° C. Since 30° C is a very high wastewater temperature for all but the most southerly States in the United States, a summary of relative rates in terms of other maximum temperatures is as shown in table I-1, based on the data of figure I-13.

These data indicate, on the basis of temperature alone and the most adverse conditions considered possible, that up to five times as much detention time may be needed to accomplish complete nitrification in the winter as is needed in the summer. Temperature effects can be overcome to a considerable degree, however, by increasing mixed-liquor suspended solids (MLSS) and adjusting pH to more favorable levels. Optimum design for complete nitrification will depend on the best combination of aeration tank capacity, MLSS, and pH for winter operating conditions. Under summer conditions, operation will be possible at less favorable pH levels and lower MLSS.

Discussion

When all of the foregoing information is evaluated, rates of nitrification can be computed. The rate of nitrification has been defined as the weight ratio of ammonia nitrogen oxidized per day to the MLVSS.

The rates for any pH within the range of 6.0 to 10.5 are shown in figure I-14. All rates are for a temperature of 20° C. As the figure shows, the rate varies from a maximum of 0.185 gram NH_3-N nitrified per day per gram MLVSS at a pH of 8.4 to a minimum of 0.020 gram NH_3-N nitrified per day per gram MLVSS at a pH of 6.0.

The results obtained in this study with respect to pH show good correlation with the results indicated in the section of the paper on work performed by others.

This study obtained results on temperature effects opposed to those observed at Ann Arbor, Mich., reported by Borchardt,[10] and shown in figure I-4. Borchardt's low-temperature observations were made in extended aeration studies by measuring the ammonia and nitrate oxygen in the effluent of the units. It is felt that the apparent effects of temperature were observed because the units were not being stressed to their limit of nitrification at the higher temperatures and

Table I-1.—*Relative rates of nitrification at various temperatures*

30° C	25° C	20° C	15° C	10° C	5° C
100	80	60	48	[1]27	[1]12
	100	75	60	34	[1]16
		100	80	45	21

[1]Abnormal temperatures for maximums stated.

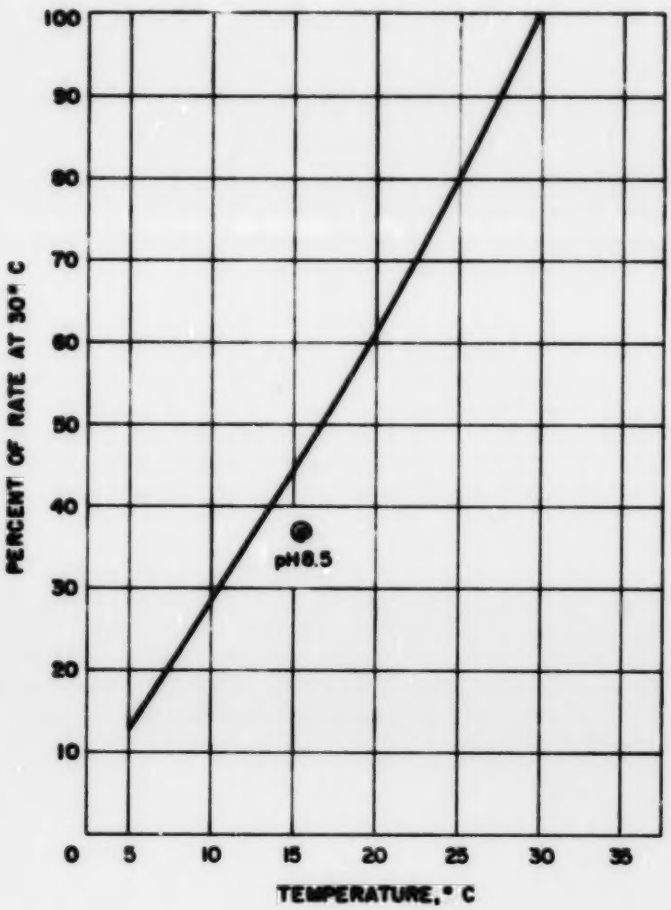

Figure I-13. Rate of nitrification at all temperatures compared to rate at 30° C.

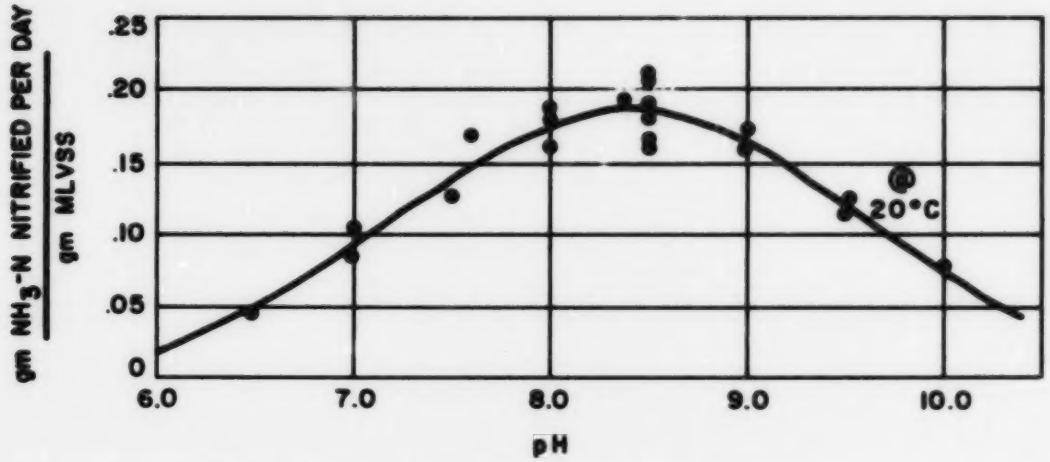

Figure I-14. Rate of nitrification versus pH at constant temperature.

complete nitrification was being obtained in less time than the detention time of the units. As the temperature decreased, the time required to obtain complete nitrification approached the detention time of the units; when the temperatures dropped low enough, the time required for complete nitrification exceeded the detention time and this lower percent of nitrification was noted. Results of this study are from units that were stressed to their capacity at all times, and indicated an immediate drop in efficiency as the temperatures decreased in agreement with results reported by Sawyer and Rohlich.[11]

Figure I-15 gives the expected rate of nitrification compared to temperature for various selected pH conditions. This figure allows the computation of the time required for complete nitrification at any MLVSS concentration, ammonia-nitrogen concentration, temperature, and pH.

The curve at the optimum pH of 8.4 was determined from information gathered during the course of the study. The curves for 75 percent and 50 percent of the optimum rates were computed from the rates experienced at pH 8.4. The pH values for the 75-percent and 50-percent curves were obtained from figure I-11.

From a practical standpoint, figure I-15 indicates that if the nitrification system were run at 50 percent of the optimum conditions, the time required to completely oxidize the ammonia nitrogen would double or the MLVSS would have to be carried at twice the level necessary for complete nitrification under optimum conditions.

Summary

The foregoing may be briefly summarized as follows:

- The ammonia-nitrogen concentration did not inhibit nitrification in concentrations of less than 60 mg/l.
- pH did affect the rate of nitrification. Optimum pH was found to be 8.4.

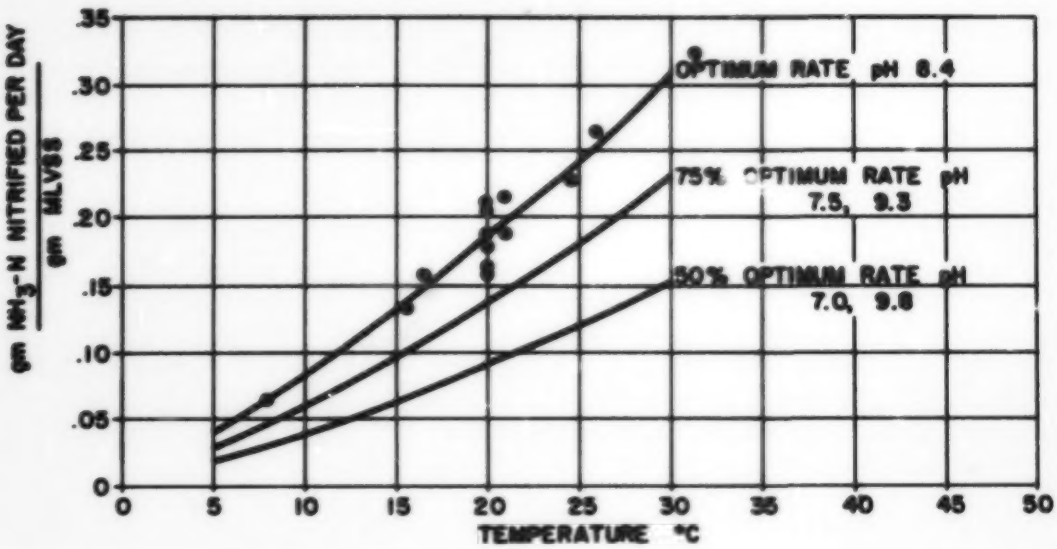

Figure I-15. Rate of nitrification versus temperature at various pH levels.

- Temperature did affect the rate of nitrification. The rate increased through the range of 5° to 30° C, in reasonable agreement with the van't Hoff-Arrhenius law.
- The time required for nitrification is directly proportional to the amount of nitrifiers present in the system.
- Instantaneous increases (from 50 to 110 mg/l) or decreases (from 50 to 5 mg/l) in BOD concentration did not affect the rate of nitrification. It would be expected, however, that a change in the average BOD concentration of the feed would affect that percentage of MLVSS which is composed of nitrifiers, and as a result would affect the time to achieve complete nitrification.

OXYGEN NITRIFICATION SYSTEMS*

From 1971 through 1973, Union Carbide Corporation conducted numerous nitrification studies utilizing pure oxygen. Included were pilot-plant operations at Tampa, Fla., Amherst, N.Y., and Brockton, Mass., and a number of laboratory treatability studies. Data from the studies have been incorporated into the development of a design approach for oxygen nitrification systems.

These oxygen nitrification studies have shown that the concentration of *Nitrosomonas* is proportional to the concentration of influent ammonia. As the ammonia loadings to the system increase, the relative population of nitrifying organisms to total volatile suspended solids will also increase. Because the nitrifying organisms are a small fraction of the total volatile suspended solids, the nitrifying capacity of a system can increase substantially owing to an increase of ammonia in the influent without a noticeable change in the MLVSS.

*Abstracted from M. J. Stankewich, Jr., Union Carbide Corporation, "Biological Nitrification with the High Purity Oxygenation Process," presented at the Annual Meeting of the Purdue Industrial Waste Conference, Lafayette, Ind., May 1972.

Although nitrifying organisms initially prefer a pH environment of 7.0 to 8.0, the Union Carbide oxygen studies reveal that they will acclimate to lower pH environments and approach the ammonia removal capacity attainable at the higher pH levels. Acclimation was demonstrated by the fact that, after a period of time, consistent nitrification was achieved at operating conditions at which nitrification would fail before acclimation.

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[3]D. Jenkins and W. E. Garrison, "Control of Activated Sludge by Mean Cell Residence Time," *J. Water Pollut. Cont. Fed., 40*, 1905, 1968.

[4]Meyerhof, *Arch. f. die ges Physiologie, 166*, 255, 1917.

[5]M. S. Engel and M. Alexander, "Growth and Autotrophic Metabolism of *Nitrosomonas europaea*," *J. Bact., 76*, 217, 1958.

[6]Meyerhof, *Arch. f. die ges Physiologie, 164*, 416, 1916.

[7]R. E. Bragstad and L. Bradney, "Packing House Waste and Sewage Treatment at Sioux Falls, South Dakota," *Sewage Works J., 9*, 959, 1937.

[8]A. L. Downing, H. A. Painter, and G. Knowles, "Nitrification in the Activated Sludge Process," *J. Inst. Sewage Purif. (Brit.), pt. 2*, 130, 1964.

[9]A. E. Zanoni, "Secondary Effluent Deoxygenation at Different Temperatures," *J. Water Pollut. Cont. Fed., 41*, 640, 1969.

[10]J. A. Borchardt, "Nitrification in the Activated Sludge Process," *Bull. The Activated Sludge Process*, University of Michigan, Division of Sanitary and Water Resources Engineering, Ann Arbor, Mich.

[11]C. N. Sawyer and G. A. Rohlich, "The Influence of Temperature upon the Rate of Oxygen Utilization by Activated Sludge," *Sewage Works J., 11*, 946, 1939.

Chapter II

DESIGN CRITERIA OF NITRIFICATION SYSTEMS

This chapter discusses the design criteria that appear to be reasonable at this time (October 1972). It must be emphasized that these criteria are based solely on pilot-plant experience.

NITRIFICATION TANKS

Tank Layout

Because the rate of oxidation of ammonia is essentially linear (zero-order reaction), short circuiting must be prevented. The tank configuration should insure that flow through the tank follows the plug-flow mixing model as closely as possible. Such configuration can be accomplished by dividing the tank into a series of compartments with ports between them. Figure II-1 shows three compartments as a minimum number. Tanks can be designed for either diffused-air or mechanical-aeration systems.

Since the oxidation rate of the process varies widely with temperature, special provisions may be necessary to incorporate the necessary flexibility in the oxygen supply system, as discussed hereinafter.

pH Control

Nitrification tanks should be sized to permit complete nitrification under the most adverse combination of ammonia load and temperature expected, and at a pH as near optimum as feasible. The range of 7.6-7.8 is recommended in order to allow carbon dioxide to escape to the atmosphere.

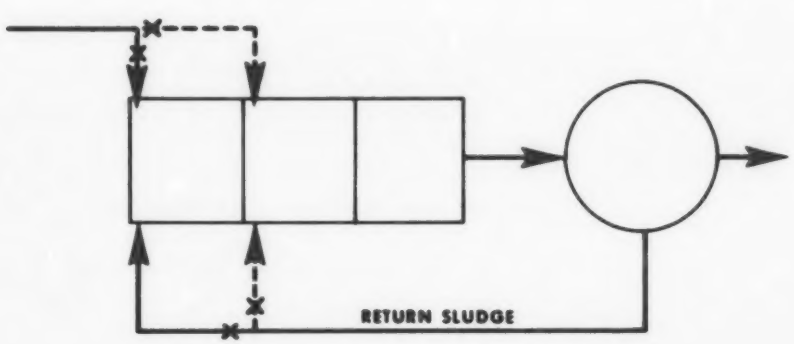

Figure II-1. Model nitrification system.

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The nitrification process destroys alkalinity and the pH may fall to levels that will inhibit nitrification unless excess alkalinity is present in the wastewater or lime is added to maintain favorable pH levels.

$$2NH_4HCO_3 + 4O_2 \rightarrow 2HNO_3 + 4H_2O + 2CO_2$$

$$2HNO_3 + Ca(HCO_3)_2 \rightarrow Ca(NO_3)_2 + 2CO_2 + 2H_2O$$

$$2NH_4HCO_3 + 4O_2 + Ca(HCO_3)_2 \rightarrow Ca(NO_3)_2 + 4CO_2 + 6H_2O$$

Theoretically, 7.2 pounds of total alkalinity are destroyed per pound of ammonia nitrogen oxidized to nitrate. One-half of this destruction is due to loss of alkalinity caused by ammonia and the remainder is due to destruction of natural alkalinity, as shown in the foregoing equations.

Whether lime additions will be required depends upon the alkalinity of the wastewater and the desired pH of operation. For operation under the most adverse temperature conditions and at operating pH, sufficient lime must be added initially to raise the pH into the desired range, and then 5.4 pounds of hydrated lime per pound of ammonia nitrogen will be required to maintain the pH. An actual titration test should be conducted to obtain design criteria. In Boston sewage, about 250 pounds of hydrated lime are needed per million gallons to raise the pH initially to optimum pH range, and an additional 700 pounds are needed to hold it there during the course of oxidation of the ammonia. The total hydrated lime requirements are estimated to be about 115 mg/l. Additional amounts of lime may be required if chemicals, such as alum, have been added previously for phosphorus removal.

Marked reductions in lime requirements will result in any system that can be designed to operate at pH levels of 7.8 or less, because carbon dioxide resulting from destruction of alkalinity and organic matter will be washed out of the liquid phase by air contact. The pH of such systems will vary somewhat with the rate of aeration (ventilation).

The type and sensitivity of the pH control system will depend on the character of the wastewater and the variations in the ammonia load fed to the system. Figure II-2 shows a proposed system for pH control in the most demanding situation. In many situations, a lesser degree of control will be feasible; in some none will be needed.

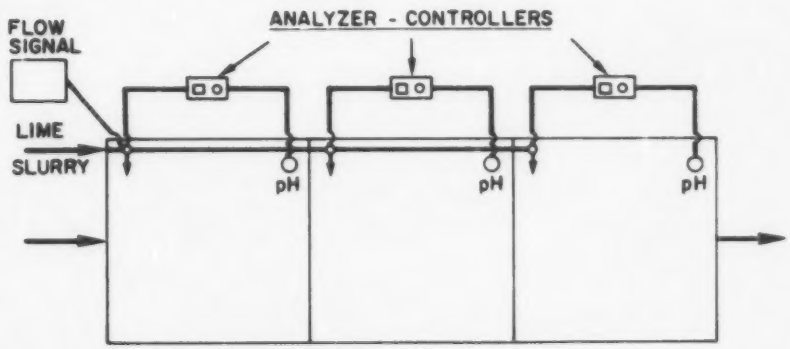

Figure II-2. pH control for nitrification system, plan view.

Although studies by the authors showed the optimum pH for the nitrification reaction to be in the range of 8.4 to 8.6, other workers have reported lower optimum levels more in keeping with those found by Engle and Alexander, as shown in Figure I-2.

Downing and Knowles[1] have reported that pH levels above 7.2 do not increase the rate of nitrification. They presented an equation

$$\text{Activity} = 1 - 0.83(7.2 - \text{pH})$$

for calculation of activity at ph levels below 7.2. Using this equation the activities in Table II-1 can be determined.

Haug and McCarty[2] recently have reported upon nitrification in submerged filters and observed pH phenomena. They found that the nitrifying organisms were able to acclimate to low pH levels of 6.0 within about 10 days, and develop the ability to oxidize ammonia as rapidly as at pH levels of 7.0 or more. They made no studies, however, on nitrifying populations in the fixed growths, so it was not proven whether the increased activity was due to acclimation or an increased population of organisms, resulting in the availability of excess ammonia.

The information provided by Downing and Knowles and Haug and McCarty offers some hope that the addition of lime for initial pH elevation may not be necessary. The need for lime then revolves around having sufficient alkalinity present to allow complete nitrification at satisfactory kinetic rates at the lowest temperatures and highest mass loadings of ammonia expected.

In any event, sufficient alkalinity should be present to leave a residual of from 30 to 50 mg/l after nitrification is completed. As a general rule, where phosphorus removal is accomplished in the first stage of a two- or three-stage system by use of alum or ferric salts, it will be necessary to provide lime-feeding facilities, and the optimum pH of operation becomes more or less an academic matter. In situations where feeding of lime is not essential, good engineering normally will indicate that additional tankage be provided to overcome the limitations of reduced activity, as opposed to providing lime-feeding facilities to keep the tankage at a minimum.

Table II-1.—*Activities at pH 7.2 and below*

pH	Activity
7.2	1.00
7.0	.83
6.8	.67
6.6	.50
6.4	.34
6.2	.17

MLSS and MLVSS Concentrations

Designs based on MLSS concentration alone should be avoided, because MLSS will not truly reflect the biological mass in the system. The ratio of MLVSS to MLSS may vary depending on the nonvolatile suspended solids (including residual chemical precipitates) in the feed. The fraction of the MLVSS attributable to nitrifying organisms is as yet unknown; however, for nitrification systems receiving normal secondary effluents, MLVSS concentrations of 1,500-2,000 mg/l appear to be safe for design.

Tank Capacity

The choice of the design-peak load depends on the circumstances of the specific project, and need not necessarily be the absolute maximum expected load. For many projects, the use of a peak-load factor of 1.5 represents a reasonable peak at low-temperature conditions.

Figure II-3 shows the permissible volumetric loading of the nitrification tanks at a pH of 8.4 and at various temperatures and MLVSS concentrations, based on the nitrification kinetics studies at Marlborough, Mass. (see chapter I).

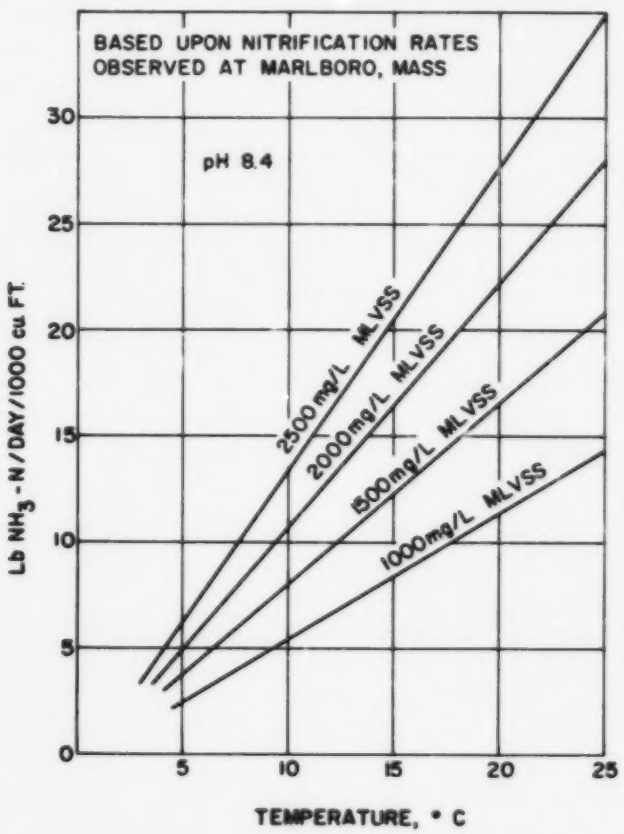

Figure II-3. Permissible nitrification-tank loadings.

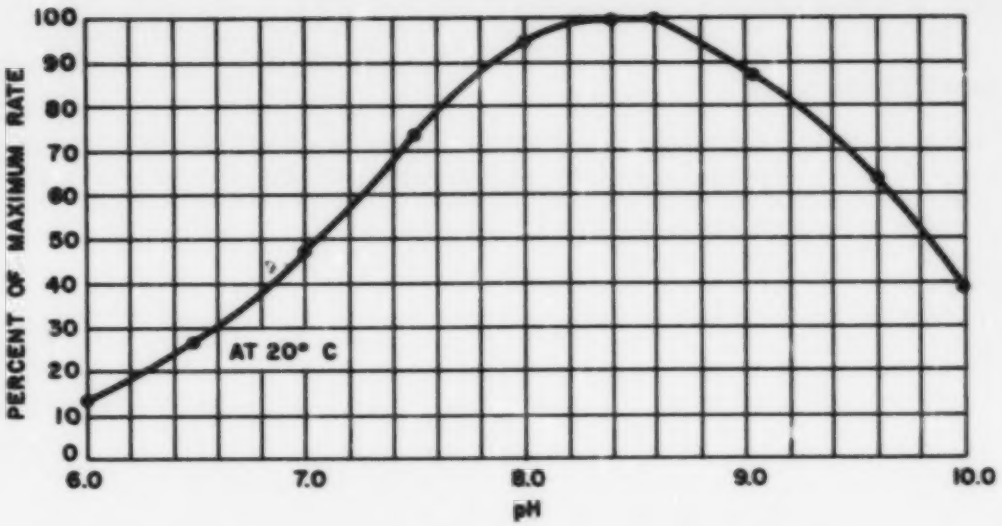

Figure II-4. Percent of maximum rate of nitrification at constant temperature versus pH.

Figure II-4 shows the corrections that must be applied to the permissible loadings when the pH is different from 8.4. In plants with well-buffered wastewater, it may be more economical to provide the additional tankage to permit operation at a lower pH, rather than to add an alkaline material. The following is a sample calculation for computing the tank size:

Given:

Design flow = 10 mgd

Average concentration to nitrification tanks = 15 mg/l

Minimum temperature = 10° C

Operating pH = 7.8

MLVSS concentration = 1,500 mg/l

Computed:

1. NH_3 load

   a. Average = 10 X 8.34 X 15 = 1,250 lb/day

   b. Maximum = 1,250 X 1.5 = 1,870 lb/day

2. Tank volume at 10° C, MLVSS = 1,500 mg/l

   a. From figure II-3, volumetric loading = 8.2 lb per 1,000 ft^3

   b. Tank volume = 1870/8.2 X 10^3 = 228,000 ft^3

3. Tank volume adjusted to pH 7.8 (see fig. III-4) = 228,000/0.88 = 260,000 ft^3

4. Check detention period = (260,000 X 24 X 7.48)/(10 X 10^6) = 4.65 hr

Oxygen Requirements

Stoichiometrically, each pound of ammonia nitrogen that is nitrified requires 4.6 pounds of oxygen. (The amount of ammonia nitrified is usually slightly more than the amount of nitrate measured because some denitrification occurs.) Usually, it is assumed that all of the ammonia fed will be nitrified. An additional oxygen allowance must be made for carbonaceous BOD that escapes from the secondary treatment process.

Nitrification appears to be uninhibited at DO concentrations of 1 mg/l or more. Design based on maintaining 3 mg/l of DO in the mixed liquor under average loading conditions includes a reasonable factor of safety. Under peak loading the DO concentration may be permitted to fall somewhat, but not below 1 mg/l.

There follows a sample calculation for oxygen requirements:

Given:

Design flow = 10 mgd

Average NH_3-N concentration = 15 mg/l

Average BOD = 30 mg/l

Computed:

1. NH_3 load
   a. Average = 1,250 lb/day
   b. Maximum = 1,870 lb/day
2. BOD load = 2,500 lb/day
3. Oxygen requirement
   a. NH_3 oxidation = 1,870 X 4.6 = 8,650 lb/day
   b. BOD requirement = 2,500 X 1.5 = 3,750 lb/day
   c. Total requirement = 12,400 lb/day

To design the aeration system, the total oxygen requirement must be corrected to actual operating conditions by the use of well-known equations incorporating such factors as

- Critical wastewater temperature
- Minimum DO concentration
- Coefficient of wastewater oxygen-uptake rate (alpha)

- Coefficient of wastewater DO saturation (beta)
- Altitude of plant

The rate of nitrification will vary significantly with temperature and pH, and compensation for this variation must be made in the design of the plant. During the summer, the following methods can be used to match the oxygen demand rate to the oxygen supply rate:

- Reduce MLSS concentration
- Reduce pH by reducing chemical supply
- Reduce tankage in service while increasing oxygen supply to the tanks remaining in service

Miscellaneous

Although the nitrification process will handle the normal variations in ammonia load found in raw wastewater, experience at the Washington, D.C., pilot plant indicates that nitrification in the carbonaceous removal units must be carefully controlled to insure stable operation. Experience at South Lake Tahoe, Calif., indicates that the addition of 2-8 mg/l of chlorine to the effluent of the carbonaceous aeration tank effectively will prevent nitrification. In addition, excessive amounts of carbonaceous BOD and suspended solids that escape from the carbonaceous treatment process, such as those associated with "bulking" sludge caused by filamentous growths, must not be so great that sludge wasting from the nitrification process causes a washout of the nitrifying organisms. Carbonaceous-BOD concentrations higher than 50 mg/l in the nitrification influent may interfere with winter operation.

Foam spray systems have not been found necessary where the MLSS concentration was greater than 2,000 mg/l.

The following substances have been shown[a] to have an inhibiting effect on the nitrification process in concentrations greater than those indicated:

Halogen-substituted phenolic compounds, 0 mg/l

Thioures and thioures derivatives, 0 mg/l

Halogenated solvents, 0 mg/l

Heavy metals, 10-20 mg/l

Cyanides and all compounds from which hydrocyanic acid is liberated on acidification, 20 mg/l

Phenol and cresol, 20 mg/l

SETTLING TANKS

Design information on settling tanks serving nitrification systems is limited generally to pilot-plant research studies. The criteria given herein represent what has been determined as of October 1972.

[a]E. A. Drew, Chief Engineer, Middle Regional Drainage Scheme, England.

Surface Loadings

The maximum permissible hydraulic surface loading appears to be approximately 1,000 gpd/ft^2. Average surface loadings should be in the range of 400-600 gpd/ft^2. It may be necessary to reduce this loading somewhat if the MLSS concentration is greater than 2,500 mg/l, because of limiting sedimentation-tank-solids loadings.

Mulbarger[b] noted at the Manassas, Va., pilot plant that settling improved in the nitrification settling tanks when alum was added to upstream processes, probably due to carryover of alum floc. It has also been noted that the periodic addition of waste sludge from the carbonaceous treatment process improves settling. In cases where nitrification units follow, addition of waste sludge from them may facilitate a more rapid buildup of nitrifying organisms.

Number of Tanks

Because of the relatively slow growth and settling rates of nitrifying sludges, it is desirable to provide more than two settling tanks to insure that the sludge is kept within the system when a tank is down for maintenance and repair. Four tanks are a desirable minimum number.

Depth

Depths of 12-15 feet are recommended.

Sludge-Collection Equipment

Experiences to date have shown no evidence of rising-sludge problems, probably due to complete nitrification and very low residual BOD_c (oxidizable carbonaceous matter) levels. Use of rapid-removal suction-type sludge-collection equipment is not mandatory, but it may be desirable in large circular tanks. The settling tanks should be equipped with skimmers and provision should be made to use the scum system to pump floating sludge, should it ever occur, to the nitrification tank influent.

Sludge

It is recommended that capacity be provided for a return-sludge rate of 50-100 percent of average flow, since the nitrification sludge is lighter and does not compact as well as carbonaceous sludges.

Continuous sludge wasting was not normally necessary at the pilot plants at Washington, D.C., and Marlborough, Mass. Periodic adjustments of MLSS concentration are necessary, however, and provisions should be made to dispose of waste nitrification sludge with the waste sludge from the carbonaceous treatment process.

REFERENCES

[1]Downing and Knowles, *Proceedings of the Third International Conference on Water Pollution Research*, vol. 2, p. 117, Munich, 1966.

[2]Haug and McCarty, *J. Water Pollut. Cont. Fed.*, *44*, 2089, 1972.

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[b]M. C. Mulbarger, private communication.

Chapter III

DENITRIFICATION BY SUSPENDED GROWTH SYSTEMS

Only pilot-plant data are available at the present time to serve as the basis of suspended growth denitrification systems. It appears that the most valid information that can serve as a basis of rational design comes from the pilot-plant studies at Manassas, Va.,[a] and the investigations at Washington, D.C.[b] Figure III-1 shows the kinetics of the denitrification reaction in relation to temperature for a given pH range, as reported by Mulbarger and as observed at Washington, D.C. The data from which the figure was developed were obtained in laboratory studies in a manner comparable to those shown in figure I-15, and are considered fully as reliable. The reasons for the difference between the two curves has not been determined fully; but this unexplained difference points to the need for additional kinetic studies on other wastewaters.

DENITRIFICATION TANKS

The tank layout should assure that the plug-flow mixing model is followed as closely as possible, because nitrates are not adsorbed by biological growths and detention periods may be quite short. Whether covered tanks are required to minimize absorption of oxygen from the atmosphere is a matter of conjecture. There is some evidence to indicate that properly designed denitrification units can be made to seal themselves by formation of a floating scum. In any event, airtight or walk-in covers are to be avoided, because nitrogen and carbon dioxide are both released during the denitrification reaction.

pH

Studies by Mulbarger[c] have indicated that optimum pH for the denitrifying organisms is in the range of 6.5-7.5, the same as for most saprophytic bacteria. Figure III-2 shows the corrections that must be applied to the permissible tank loading when the pH is different from the optimum range.

That the pH of the effluent from the nitrifying units may exceed 7.5 at some time during a year is no particular problem, because carbon dioxide generated from oxidation of carbonaceous matter in the denitrification unit quickly reduces the pH into the favorable range below 7.5. There is no need for addition of chemicals to control pH.

MLSS and MLVSS

The limited experience available has shown that denitrifying sludges have settling properties comparable to good activated sludges. It seems reasonable to assume, therefore, that mixed-liquor solids in the range of 2,000 to 3,000 mg/l can be maintained without excessive rates of returning sludge. The volatile matter in the denitrifying sludges at Manassas, Va., and Washington, D.C., is about 65 percent.

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[a] Reported by M. C. Mulbarger, private communication.
[b] J. Stamberg, private communication.
[c] M. C. Mulbarger, private communication.

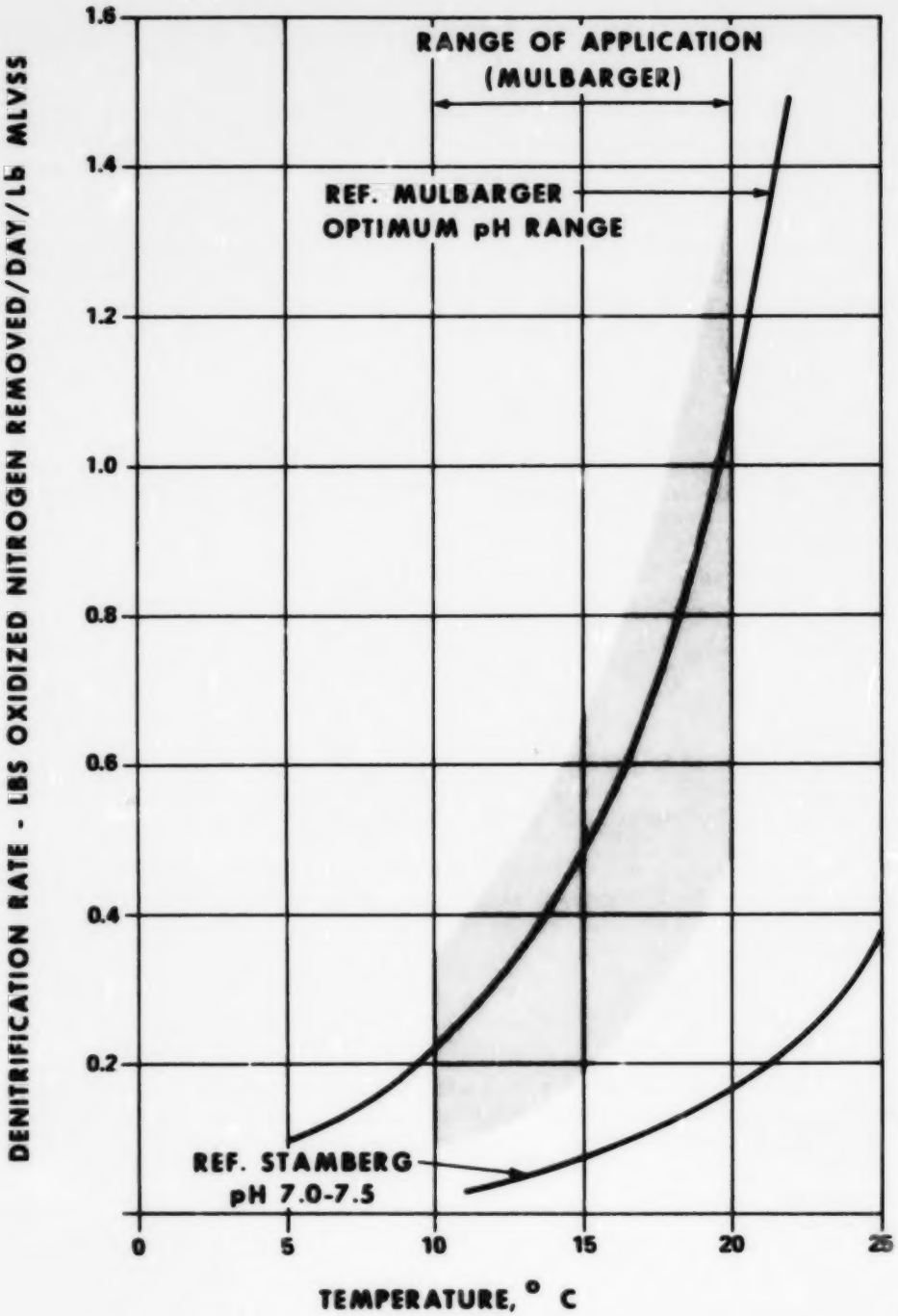

Figure III-1. Effect of temperature on rate of denitrification.

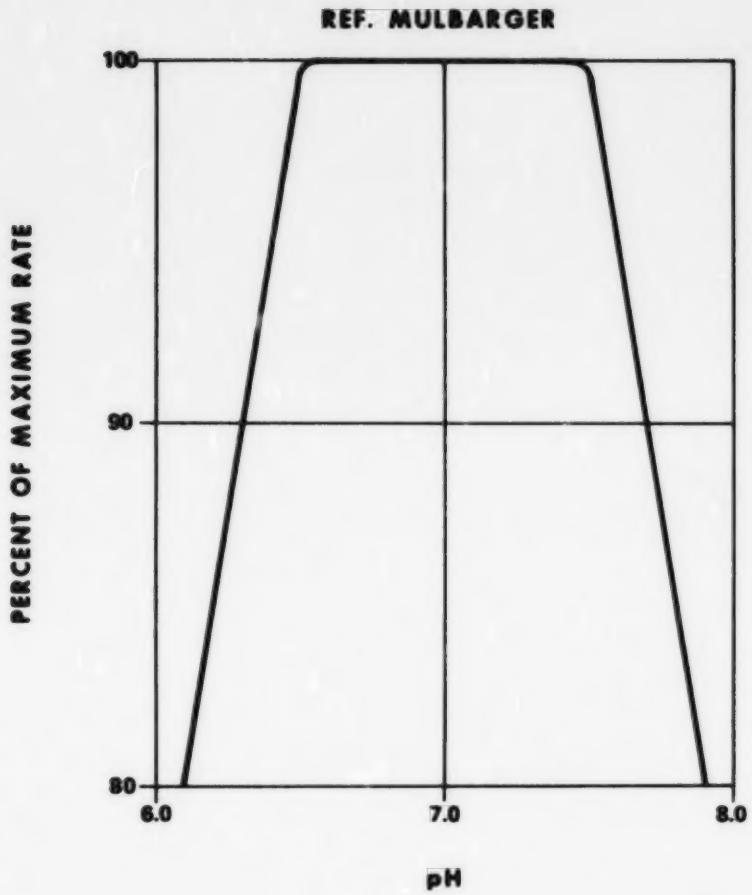

Figure III-2. Percent of maximum rate of denitrification versus pH.

Size

Reference to figure III-1 will show that the minimum temperature to be allowed for will play a great role in determining the size of the denitrification tanks, as well as the MLVSS that can be carried in the system. Figure III-2 and figure III-3 may be used to compute the size of the denitrification tanks as follows (sample calculation based on kinetic data from Manassas, Va.):

Given:

Design flow = 10 mgd

Average NO_3-N + NO_2-N concentration = 15 mg/l[d]

Minimum temperature = 10° C

Expected operating pH = 7.3

[d]For this example problem, assume complete conversion is desired.

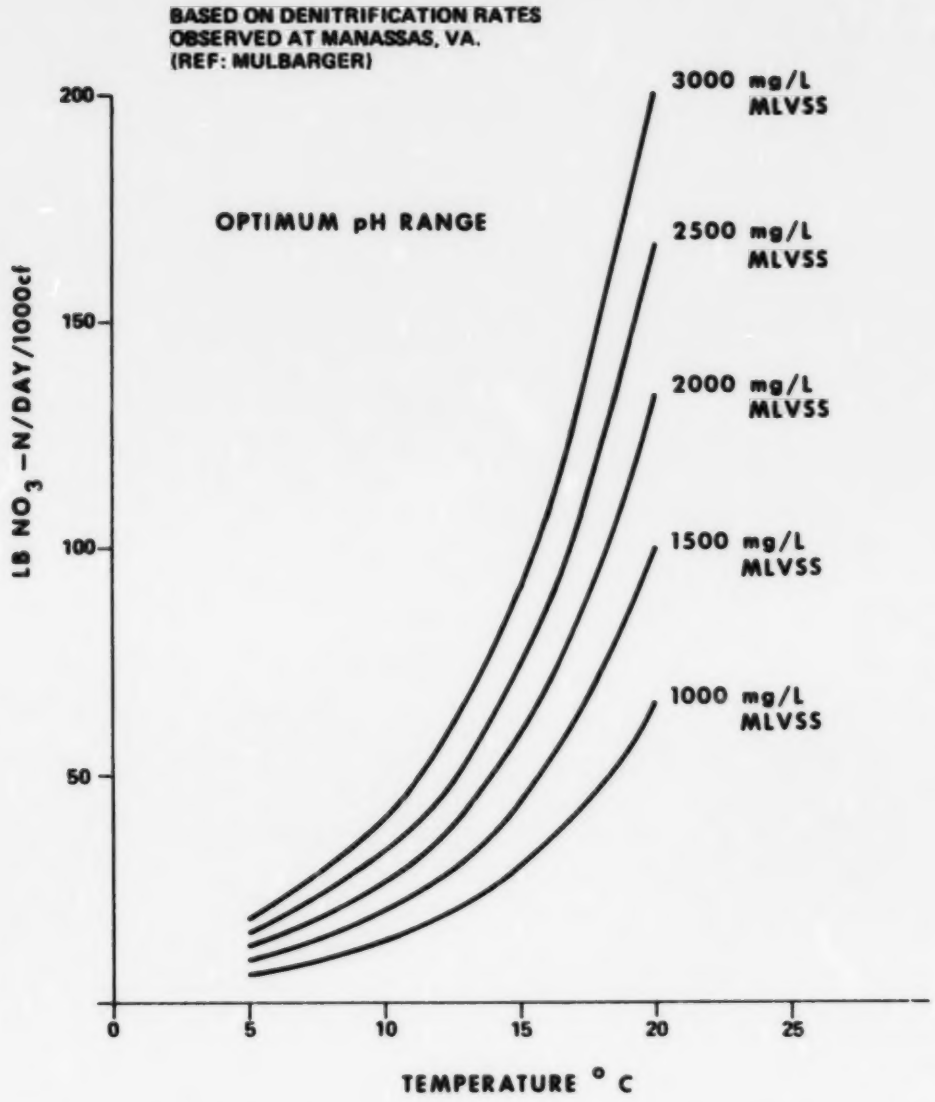

Figure III-3. Permissible denitrification-tank loadings.

MLVSS = 2,000 mg/l

Computed:

1. NO_3-N + NO_2-N loading

   a. Average = 10 X 8.35 X 15 = 1,250 lb/day

   b. Peak = 1,250 X 1.5 = 1,870 lb/day

2. Tank loading at 10° C, optimum pH (from fig. III-3) = 26.8 lb/1,000 ft^3

3. Tank volume at MLVSS = 2,000, optimum pH = $1,870/26.8 \times 10^3 = 70,000$ ft^3

4. Check detention period = $(70,000 \times 7.48 \times 24)/10$ mgd = 1.25 hr

Such a system would have over twice the tankage needed at 20° C. For this reason, good design will allow for idle operation of part of the capacity during the warm months of the year. A design similar to that shown for the nitrification system in figure II-1 is recommended.

At Washington, D.C., the results of Stamberg indicate that the tankage allowance must be considerably more generous—possibly three or four times as great if complete denitrification is to be required in the winter months. It is questionable whether denitrification will be needed during the low-temperature months of the year, because of the flushing action of high river flows during the spring months.

Carbonaceous Matter

Effluents from nitrifying units are exceptionally free of BOD_c. For this reason, denitrification is very slow unless a readily oxidizable source of carbonaceous matter is added. Methyl alcohol (methanol) is the cheapest commercial source of carbonaceous matter at this time. Glucose (corn sugar) is the next cheapest source. Methanol is preferable because it is more completely oxidized than glucose and, consequently, produces less sludge for disposal.

In some areas, nitrogen-deficient industrial wastes, such as brewery wastes, might be available and suitable for use. All such waste materials should be employed before considering methanol because it is produced from natural gas, which is not an unlimited resource.

When methanol is used for denitrification the basic reaction involved is

$$5CH_3OH + 6H^{+1} + 6NO_3^- \longrightarrow 5CO_2 + 3N_2 + 13H_2O$$

$$(5 \times 32) = 160 \qquad (6 \times 14) = 84$$

From the foregoing equation and weight relationships, it might be concluded that each pound of nitrate nitrogen would require about 2 pounds of methanol for its reduction, which is true, but some of the methanol is used to produce new cell growth (sludge) as follows:

$$(CH_3OH)_x \longrightarrow CO_2 + (CH_2O)_x + H_2O$$

Also, nitrified effluents normally carry some DO into the denitrification tank and some DO may enter the mixture as a result of agitation. This increases the amount of methanol required. An equation commonly used to estimate methanol requirements is: pounds per day methanol = 2.47 lb NO_3-N + 1.53 lb NO_2-N + 0.87 lb DO.

Reports indicate that from 3 to 4 pounds of methanol per pound of nitrate nitrogen are required to consume DO and leave sufficient to reduce the nitrate to nitrogen gas.

The amount of methanol fed must be very closely controlled by a system such as that shown in figure III-4 to insure that enough is fed to reduce the nitrates and to avoid an excess. Any excess is not only a waste of chemical; it creates an undesirable residual BOD.

Equipment

The contents of the denitrification tanks are mixed with underwater mixers comparable to those used in flocculation tanks in water-treatment plants. The energy provided must be sufficient

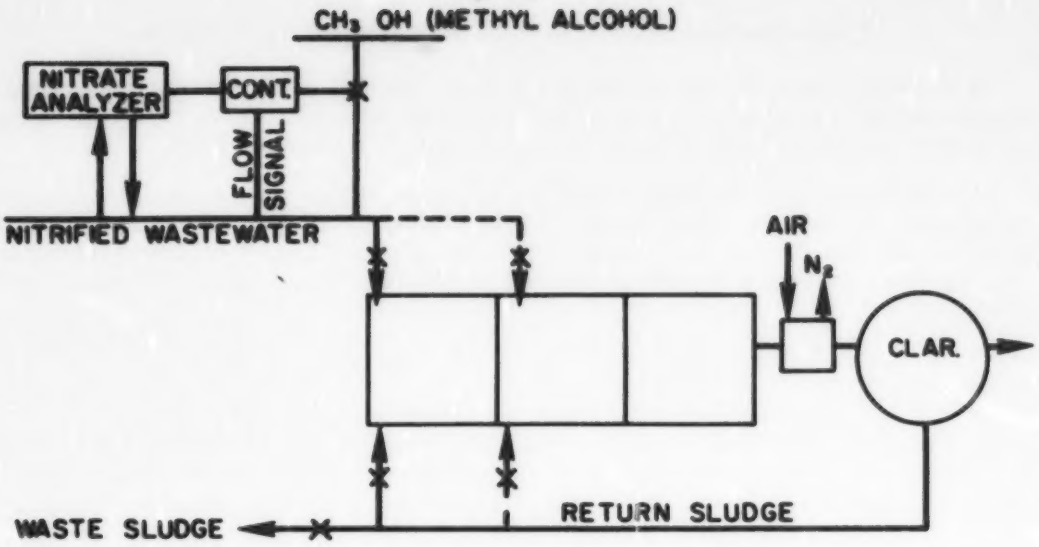

Figure III-4. Model system for feeding methyl alcohol to denitrification tanks.

to keep the MLSS in suspension, but must be controlled to prevent pickup of atmospheric oxygen as much as possible, unless the tanks are covered or some other method is used to exclude contact with the air.

Power requirements of ¼-½ hp per thousand cubic feet have been found to be adequate.

Nitrogen Release

The denitrification reaction results in the formation of carbon dioxide and nitrogen gas. Both have limited solubility in water, especially the latter. Because of the gentle mixing used in the denitrification tanks, the mixed liquor leaving the tanks is supersaturated with nitrogen, and possibly carbon dioxide. As a result, gas bubbles tend to form and adhere to the MLSS and inhibit settling in the final clarifier. Supersaturated conditions can be relieved by employing an aeration tank or aerated open tanks. It is recommended that from 5 to 10 minutes detention be provided at peak flow. Such a facility will also provide the ability to remove small amounts of excess methanol.

SETTLING TANKS

The limited experience available indicates that the settling properties of denitrification sludge, following relief of supersaturation, are very similar to conventional activated sludge.

Tank depths of 12-15 feet are recommended, and surface overflow rates should not exceed 1,200 gallons per square foot per day at peak flows. MLSS concentrations greater than 2,500 mg/l may require larger tanks owing to the higher settling-tank solids loadings.

A suction-type sludge collector is recommended for large circular tanks. Long rectangular tanks should be equipped with midtank sludge-drawoff systems.

Skimming facilities should be provided on the settling tanks and provisions should be made for returning the scum to the denitrification tank when desired.

SLUDGE

Return

Capability of returning sludge to the denitrification tank of up to at least 50 percent and preferably of up to 100 percent of average flow is recommended.

Waste

Provision should be made for periodic wasting of sludge from the denitrification systems similar to that employed for carbonaceous systems. Normally, the sludge should be wasted to mix with primary and/or waste-activated sludge and be disposed of with them. The waste-sludge line, however, should be designed to transport sludge to the nitrification tank when desired. In the event that nitrifying sludge is lost from the nitrifying system, it is normally captured by the denitrifying system. It can be returned to its normal home, at least in part, by using denitrifying sludge to reseed the nitrification tank.

Quantity of Waste Sludge

It is reported that about 0.2 pound of sludge will be generated for each pound of methanol fed. This would correspond to about 0.7 pound per pound of nitrate nitrogen reduced.

EFFLUENT QUALITY

Based on pilot-plant studies operating under steady-state conditions, in table III-1 effluent quality is predicted from a nitrification-denitrification system designed for operation at 10° C wastewater temperatures. At warmer temperatures improved quality can be expected.

Thus, it appears that 90 percent removals of total nitrogen can be achieved in actual practice.

Table III-1. *Predicted effluent quality at 10° C wastewater temperatures*

Component	Milligrams per liter
Suspended solids	10
BOD	5
Organic-N	1.0
NH_3-N	.5
NO_3-N	.5
Total-N	2.0

* U. S. GOVERNMENT PRINTING OFFICE : 1976 731-993/372

METRIC CONVERSION TABLES

Recommended Units

Description	Unit	Symbol	Comments	Customary Equivalents
Length	metre	m	*Basic SI unit*	39.37 in.=3.28 ft=1.09 yd
	kilometre	km		0.62 mi
	millimetre	mm		0.03937 in.
	micrometre	μm.		3.937×10^{-5}–10^{3}Å
Area	square metre	m^2		10.764 sq ft = 1.196 sq yd
	square kilometre	km^2		0.384 sq mi = 247 acres
	square millimetre	mm^2		0.00155 sq in.
	hectare	ha	The hectare (10 000 m^2) is a recognized multiple unit and will remain in international use.	2.471 acres
Volume	cubic metre	m^3		35.314 cu ft = 1.3079 cu yd
	litre	l	The litre is now recognized as the special name for the cubic decimetre.	1.057 qt = 0.264 gal = 0.81×10^{-4} acre-ft
Mass	kilogram	kg	*Basic SI unit*	2.205 lb
	gram	g		0.035 oz = 15.43 gr
	milligram	mg		0.01543 gr
	tonne or megagram	t Mg	1 tonne = 1 000 kg 1 Mg = 1 000 kg	0.984 ton (long) = 1.1023 ton (short)
Time	second	s	*Basic SI unit*	
	day	d	Neither the day nor the year is an SI unit but both are important.	
	year	year		
Force	newton	N	The newton is that force that produces an acceleration of 1 m/s^2 in a mass of 1 kg.	0.22481 lb (weight) = 7.233 poundals
Moment or torque	newton metre	N-m	The metre is measured perpendicular to the line of action of the force N. Not a joule.	0.7375 ft-lbf
Stress	pascal	Pa		0.02089 lbf/sq ft
	kilopascal	kPa		0.14465 lbf/sq in

Recommended Units

Description	Unit	Symbol	Comments	Customary Equivalents
Velocity				
linear	metre per second	m/s		3.28 fps
	millimetre per second	mm/s		0.00328 fps
	kilometre per second	km/s		2.230 mph
angular	radians per second	rad/s		
Flow (volumetric)	cubic metre per second	m^3/s	Commonly called the cumec	15,850 gpm = 2.120 cfm
	litre per second	l/s		15.85 gpm
Viscosity	pascal second	Pa-s		0.00672 poundals/sq ft
Pressure	newton per square metre or pascal	N/m^2 Pa		0.000145 lb/sq in
	kilometre per square metre or kilopascal	kN/m^2 kPa		0.145 lb/sq in.
	bar	bar		14.5 lb/sq in.
Temperature	Kelvin	K	*Basic SI unit*	
	degree Celsius	C	The Kelvin and Celsius degrees are identical. The use of the Celsius scale is recommended as it is the former centigrade scale.	$\frac{5F}{9} - 17.77$
Work, energy, quantity of heat	joule	J	1 joule = 1 N-m where metres are measured along the line of action of force N.	2.778×10^{-7} kw hr = 3.725×10^{-7} hp-hr = 0.73756 ft-lb = 9.48×10^{-4} Btu
	kilojoule	kJ		2.778 kw-hr
Power	watt kilowatt joule per second	W kW J/s	1 watt = 1 J/s	

Application of Units

Description	Unit	Symbol	Comments	Customary Equivalents
Precipitation, run-off, evaporation	millimetre	mm	For meteorological purposes it may be convenient to measure precipitation in terms of mass/unit area (kg/m^2). 1 mm of rain = 1 kg/m^2	
River flow	cubic metre per second	m^3/s	Commonly called the cumec	35.314 cfs
Flow in pipes, conduits, channels, over weirs, pumping	cubic metre per second	m^3/s		
	litre per second	l/s		15.85 gpm
Discharge or abstractions, yields	cubic metre per day	m^3/d	1 l/s = 86.4 m^3/d	1.83×10^{-3} gpm
	cubic metre per year	m^3/year		
Usage of water	litre per person per day	l/person day		0.264 gcpd
Density	kilogram per cubic metre	kg/m^3	The density of water under standard conditions is 1 000 kg/m^3 or 1 000 g/l or 1 g/ml.	0.0624 lb/cu ft

Application of Units

Description	Unit	Symbol	Comments	Customary Equivalents
Concentration	milligram per litre	mg/l		1 ppm
BOD loading	kilogram per cubic metre per day	kg/m^3d		0.0624 lb/cu-ft day
Hydraulic load per unit area; e.g. filtration rate	cubic metre per square metre per day	m^3/m^2d	If this is converted to a velocity, it should be expressed in mm/s (1 mm/s = 86.4 m^3/m^2 day).	3.28 cu ft/sq ft
Hydraulic load per unit volume; e.g., biological filters, lagoons	cubic metre per cubic metre per day	m^3/m^3d		
Air supply	cubic metre or litre of free air per second	m^3/s l/s		
Pipes:				
diameter	millimetre	mm		0.03937 in.
length	metre	m		39.37 in. = 3.28 ft
Optical units	lumen per square metre	lumen/m^2		0.092 ft candle/sq ft